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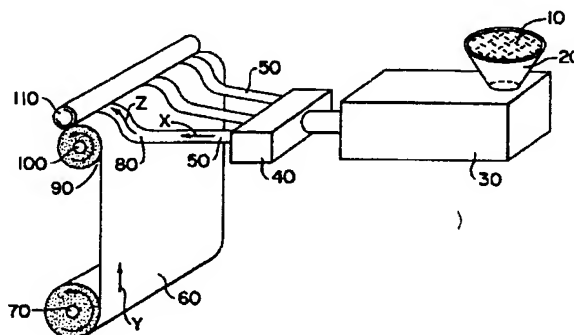
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(54) MEMBRANE CREUSE EN FIBRES - CONSTITUEE D'ALVEOLES ET DE TUBES THERMOPLASTIQUES RESISTANT AUX SOLVANTS, ET METHODES DE FABRICATION

(54) HOLLOW FIBER MEMBRANE FABRIC - CONTAINING CARTRIDGES AND MODULES HAVING SOLVENT-RESISTANT THERMOPLASTIC TUBE SHEETS AND METHODS FOR MAKING THE SAME

(57)

This invention provides spiral-wound hollow fiber membrane fabric-containing cartridges and modules for separations and other phase contact applications, including tube sheets having improved solvent resistance and mechanical durability which are fabricated by extrusion of thermoplastic resins having particular defined characteristics, and methods for making the same.





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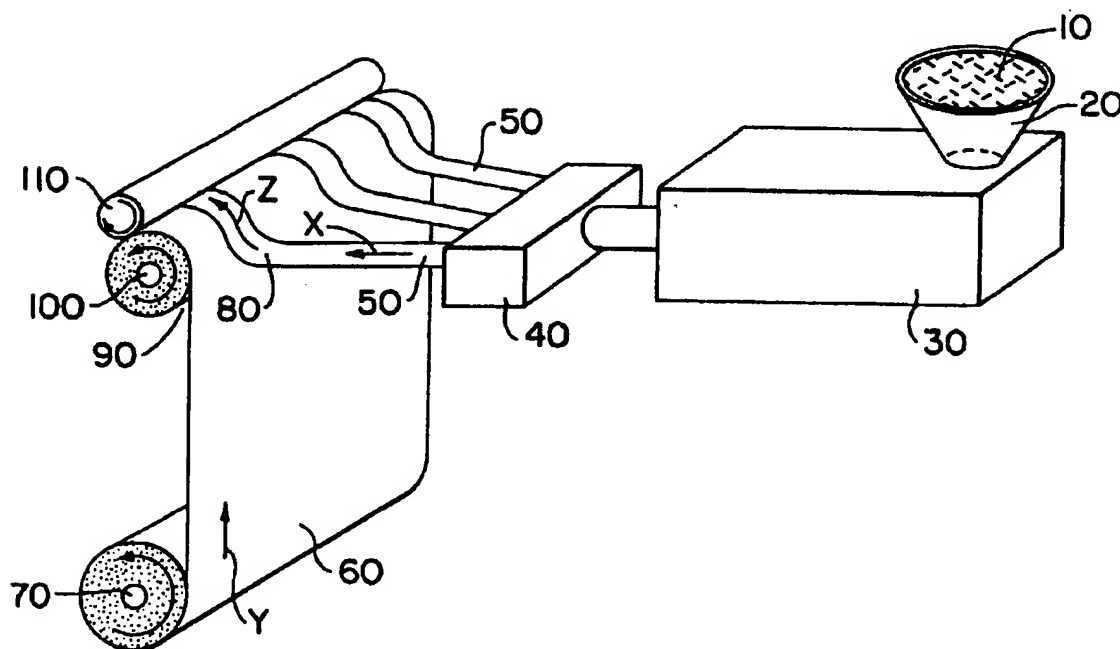
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RESISTANT AUX SOLVANTS, ET METHODES DE FABRICATION

(54) Title: HOLLOW FIBER MEMBRANE FABRIC - CONTAINING CARTRIDGES AND MODULES HAVING SOLVENT-
RESISTANT THERMOPLASTIC TUBE SHEETS AND METHODS FOR MAKING THE SAME



(57) Abrégé/Abstract

This invention provides spiral-wound hollow fiber membrane fabric-containing cartridges and modules for separations and other phase contact applications, including tube sheets having improved solvent resistance and mechanical durability which are fabricated by extrusion of thermoplastic resins having particular defined characteristics, and methods for making the same.

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Background

This invention relates to the field of spiral-type hollow fiber membrane fabric-containing cartridges and modules for separations and other phase contact applications.

- 5 In particular, this invention relates to an improved cartridge or module having tube sheets which are fabricated from solvent-resistant thermoplastic resins. The teachings of this invention can, if desired, be used in conjunction with the subject matter of applicant's U.S. Patent No.
- 10 5,264,171, entitled "Spiral-Wound Hollow Fiber Membrane Fabric Cartridges and Modules Having Flow-Directing Baffles"; and U.S. Patent No.: 5,352,361, entitled "Spiral-Wound Hollow Fiber Membrane Fabric Cartridges and Modules Having Integral Turbulence Promoters".

- 15 There is a great deal of prior art relating to the structure, fabrication and use of spiral-type hollow fiber-containing cartridges. Among the early disclosures of such devices are Mahon U.S. Patent No. 3,228,877 and McLain U.S. Patent No. 3,422,008, both of which are incorporated herein
- 20 by reference in their entirety. In general, a bundle of hollow fibers is positioned around and parallel to the longitudinal axis of a rod-shaped core (which may be a hollow mandrel and may or may not be removed after the bundle is fabricated), the ends of the hollow fiber bundle are potted
- 25 in tube sheets, and the cartridge is fitted into a pressure

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1 housing suitably ported to facilitate feed, permeate and
2 concentrate flows, to constitute a complete module.

3 More recently, the art has improved such cartridges by forming
4 the hollow fibers into a fabric-like web in which the hollow
5 fibers, parallel to the core axis, are held in place relative to
6 each other by transverse filaments which may or may not also be
7 hollow fibers. The development of these hollow fiber membrane
8 fabrics was an important step in the evolution of this technology,
9 because the fabric both makes unnecessary the manual handling of a
10 random bundle of loose hollow fibers, and facilitates the
11 construction of spiral-wound modules having the hollow fibers
12 spaced and oriented in a highly regular fashion.

13 Despite these developments, the challenge to optimize the
14 operability, efficiency and durability of these hollow fiber-
15 containing cartridges has continued. With the development of hollow
16 fiber membrane fabrics, the limiting factor in building a module
17 becomes the fabrication of the tube sheets. The classic hollow
18 fiber potting processes include gravity potting and centrifugal
19 potting. In gravity potting, a resinous potting material is
20 introduced into each of the bundle ends, one at a time, and allowed
21 to settle into the end of the bundle and cure. In centrifugal
22 potting, the bundle is inserted into the housing, the assembly is
23 spun on its midpoint to create centrifugal force at both bundle
24 ends, resinous potting material is introduced into the shell-side

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1 space near both bundle ends, and the resinous potting material is
2 allowed to cure. (See generally, Mahon U.S. Patent No. 3,228,877;
3 Maxwell et al U.S. Patent No. 3,339,341; Geary et al U.S. Patent
4 No. 3,442,002; Davis et al U.S. Patent No. 3,962,094; Operstény et
5 al U.S. Patent No. 4,369,605; and Chu et al U.S. Patent No.
6 4,865,735). Among the many drawbacks of these procedures are the
7 following: (1) these are labor-intensive manual processes; (2)
8 being manual processes, these procedures do not yield modules of
9 uniformly high quality; (3) the potting resins tend to wick along
10 the dry portions of the hollow fibers, especially in the dipping
11 process; (4) the potting resins must have a sufficiently low
12 viscosity to readily flow among the closely spaced hollow fibers
13 and wet all adjacent hollow fiber surfaces, especially in the case
14 of the centrifugal process; (5) the inherent requirement in these
15 procedures that the potting resin must readily flow among the
16 hollow fibers limits the acceptable potting resins in terms of both
17 solvent resistance and mechanical durability after cure; (6)
18 whenever the curing reaction in the potting resin is exothermic,
19 heat buildup within the tube sheet area, particularly the center of
20 the tube sheet, can lead to catastrophic meltdown of the adjacent
21 hollow fiber ends, markedly reducing the operative portion of the
22 bundle or even rendering the module useless (attempts to
23 conventionally pot a cartridge having a diameter greater than about
24 four inches will so fail, unless a resin such as an epoxy or
25 polyurethane resin having low solvent resistance, or a resin
26 including fillers (to conduct heat and/or act as a diluent,

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1 reducing the proportion of the total potting resin composition
2 which must undergo exothermic cure), is used; the low exotherm in
3 curing such a resin results in poor curing quality and accordingly
4 poor solvent resistance and/or mechanical properties); (7) gaps or
5 air bubbles in the potting resin due to inadequate flow may cause
6 leaks in the cartridge; (8) the materials conventionally used as
7 potting resins and having good solvent resistance tend to be
8 brittle (e.g., low molecular weight polyethylene); (9) the
9 materials conventionally used as potting resins and being rubbery
10 tend to have poor solvent resistance (e.g., polyurethane); and (10)
11 both the centrifugal and gravity potting techniques necessitate at
12 least one shell-side port on the side of the module housing, into
13 which the potting resin is poured. If such ports are to be used in
14 later module operation, multiple modules cannot be connected in
15 series without exterior piping or specially-designed pressure
16 housings.

17 Poor tube sheet solvent resistance and mechanical durability
18 can have great impact on the performance features of the resulting
19 modules. The feasible operating environments of the hollow fiber-
20 fabric - containing cartridges and modules ideally would include
21 all types of solvents. No hollow fiber - forming material is inert
22 to all solvents, but conventionally-available hollow-fiber spinning
23 technology does make available a wide range of hollow fiber types.
24 Assuming that one has chosen an appropriate type of hollow fiber
25 for a particular application or range of applications, and formed

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1 a fabric from the hollow fibers, poor solvent resistance in the
2 potting resin can result in failure of the cartridge or module,
3 thus limiting the capability of the hollow fibers themselves.
4 Similarly, the purpose of the tube sheets is to isolate the lumen-
5 side and shell-side portions of the cartridge or module from each
6 other. If the tube sheet material cracks or otherwise
7 disintegrates, total failure of the module occurs. Unfortunately,
8 the conventional methods of tube sheet production (centrifugal
9 casting and gravity potting), require a high degree of potting
10 resin flowability, thus limiting the range of usable potting resins
11 in terms of molecular weight, viscosity and other properties and
12 encouraging the development of solvent-induced and mechanical
13 degradation.

14 Some attempts have been made to overcome one or more of these
15 difficulties by depositing potting material to form tube sheets
16 simultaneously while the hollow fiber bundle is being formed. For
17 example, the Mahon et al U.S. Patent No. 3,755,034 discloses a
18 process in which (1) two monofilaments are continuously unwound in
19 parallel spaced-apart fashion from spools and onto a mandrel; (2)
20 one or more continuous hollow fibers are continuously unwound
21 transversely across and around the two filaments, forming a planar
22 web of hollow fibers which nearly are mutually parallel and nearly
23 are parallel to the longitudinal axis of the mandrel; (3) the web
24 is wound spirally onto the mandrel; and (4) a band of solidifiable
25 resin is applied adjacent to one or each end of the hollow fibers

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1 (near the filament) and subsequently cured to form a resinous tube
2 sheet. Epoxy resins and silicone rubbers are suggested for forming
3 the tube sheets; and the use of hypodermic needles as potting resin
4 dispensing heads is disclosed. The Schrader U.S. Patent No.
5 3,728,425 takes a different approach: (1) a single continuous
6 hollow fiber is wound transversely around an elongated cylindrical
7 mandrel core analogously to a bundle of kite string; (2) a band of
8 resin is simultaneously applied at each end of the core, forming
9 tube sheets, and is cured. Polyepoxide resin is disclosed for use,
10 and Schrader employs applicators as shown in Figure 2 to apply the
11 bands of resin. The Krueger et al U.S. Patent No. 5,059,374
12 discloses that the tube sheets may be formed about the ends of a
13 hollow fiber bundle simultaneously with laying down of the fibers,
14 such as by dripping resin along the fibers as the fibers are laid
15 down. Krueger mentions a number of materials that can serve as tube
16 sheet resins, including polyolefins and polyamides. See also,
17 Sargent et al U.S. Patent No. 3,722,695; Francisoud et al U.S.
18 Patent No. 4,343,668; applicant's copending U.S. patent application
19 serial No.: 07/816,511 entitled, "Spiral-Wound Hollow Fiber
20 Membrane Fabric Cartridges and Modules Having Flow-Directing
21 Baffles"; and applicant's copending U.S. patent application serial
22 No.: 07/917,690 entitled, "Spiral-Wound Hollow Fiber Membrane
23 Fabric Cartridges and Modules Having Integral Turbulence
24 Promoters".

1 Other prior art disclosures broadly suggesting the use of
2 thermoplastics including polyolefins as tube sheet resins have also
3 been made. For example, the Tigner U.S. Patent No. 4,138,460
4 asserts that the choice of material for potting fiber tows to make
5 tube sheets is controlled to a large extent by the viscosity
6 characteristics of the selected material, which should preferably
7 have a viscosity in the range of about 100 to about 5,000
8 centipoise at a temperature below about 150°C, and is preferably a
9 thermoplastic. Polyethylenes, polypropylenes, and copolymers and
10 mixtures thereof can be used; and reference is made to compositions
11 using low molecular weight polyethylene resins (See a similar
12 disclosure in Lipps et al U.S. Patent No. 4,211,597 and Lipps et al
13 U.S. Patent No. 4,231,871, which further note that low viscosity
14 resins tend to completely wet and encapsulate the hollow fibers in
15 shorter times and are therefore preferred). The Brauer et al, U.S.
16 Patent Reissue No. 31,389 reviews certain materials previously used
17 to fabricate tube sheets, and notes that many of them, including
18 polyolefins and olefin copolymers, have been found deficient in one
19 aspect or another. (See also, Maxwell et al U.S. Patent No.
20 3,339,341; Davis et al U.S. Patent No. 3,962,094; Zampini U.S.
21 Patent No. 4,323,453; Fritzsche et al U.S. Patent No. 4,323,454;
22 Otstot et al U.S. Patent No. 4,686,039; Opersteny et al U.S. Patent
23 No. 4,369,605; and Chu et al U.S. Patent No. 4,865,735).

24 The need continues for improved methods and materials for
25 making tube sheets which will more closely approach the solvent

1 resistance and mechanical durability of the hollow fibers
2 themselves.

3 Summary of the Invention

4 According to the invention, a method of fabricating a spiral-
5 type hollow fiber membrane fabric-containing cartridge is provided,
6 comprising the following steps:

- 7 a. forming a plurality of hollow fiber membranes each having
8 a lumen, into a fabric-like array having a warp and a
9 weft, in which the hollow fibers substantially are
10 mutually-parallel and constitute the fabric weft, and are
11 held in spaced-apart relationship by filaments
12 constituting the fabric warp; then
- 13 b. winding the array upon an axis which is substantially
14 parallel to the hollow fibers into a spirally-wound
15 membrane bundle having two bundle ends and a cylindrical
16 exterior surface; and
- 17 c. simultaneously with step (b.), extruding in molten form
18 a high-strength, solvent resistant thermoplastic resin
19 having a melting point at least about 10° Centigrade
20 below the melting point of the hollow fibers, and having
21 a melt flow index between about 0.01 to about 150
22 grams/10 minutes; and directing said resin onto each of
23 the two bundle ends to thereby pot each of the two bundle
24 ends in said resin, serving to seal the bundle end into

1 an adjacent monolithic tube sheet, a portion of the
2 bundle between the two tube sheets being free from resin
3 to form a shell-side region; and then

- 4 d. exposing the lumen ends of the hollow fibers constituting
5 at least a first one of the bundle ends to communicate
6 with the exterior of the bundle.

7 The invention also provides improved spiral-type hollow fiber
8 membrane fabric-containing cartridges, prepared by the foregoing
9 method. Further embodiments will be detailed in the discussion
10 below, and defined in the appended claims.

11 Brief Description of the Drawings

12 Figure 1 is a schematic drawing of a method for making a
13 cartridge according to the invention, in which tube sheets are
14 fabricated by extrusion of a solvent resistant thermoplastic resin
15 which is directly applied to each of the bundle ends.

16 Figure 2 is a cross sectional photograph of a tube sheet
17 prepared according to the method of Figure 1, magnified by a factor
18 of twenty with an optical microscope.

19 Figure 3 is a cross sectional photograph of a tube sheet
20 prepared according to the method of Figure 1, magnified by a factor
21 of 250 with a scanning electron microscope.

1 Figure 4 is a schematic drawing of a cartridge made according
2 to the method of Figure 1, in which the tube sheets and a perimeter
3 sealing means are simultaneously fabricated by extrusion of solvent
4 resistant resin which is directly applied to the hollow fiber
5 membrane fabric.

6 Figure 5 is a schematic drawing of a cartridge made according
7 to the method of Figure 1, in which the tube sheets and an axial
8 sealing means are simultaneously fabricated by extrusion of solvent
9 resistant resin which is directly applied to the hollow fiber
10 membrane fabric.

11 Figure 6 is a cross-sectional drawing of a module according to
12 Figure 5.

13 Detailed Description of the Invention

14 This invention provides improvements in the art of spiral-type
15 hollow fiber membrane fabric-containing cartridges and modules for
16 separations and other phase contact applications. The term "phase
17 contact" is used herein to generally describe any process involving
18 mass transfer.

19 The improvements provided by this invention primarily reside
20 in the tube sheets in which the hollow fiber membrane fabric is
21 potted. The primary purpose of this invention is to provide
22 improved solvent resistance and mechanical durability in the tube

1 sheets, and to thereby extend the utility and useful life of the
2 overall cartridges and modules. Accordingly, in the practice of
3 this invention, the tube sheets must be fabricated from a high-
4 strength, solvent resistant thermoplastic resin, and the resin must
5 be extruded at an elevated temperature to form a molten band of
6 potting material that is directed onto the surface of the hollow
7 fiber membrane fabric to be potted. In preferred embodiments, the
8 solvent resistant thermoplastic resin is a polyolefin resin. The
9 other components of the cartridges and modules can be fabricated
10 from any suitable conventionally-known materials. Preferably, such
11 other components themselves also demonstrate exceptional solvent
12 resistance and mechanical durability. Most preferably, they are
13 also fabricated from polyolefin materials.

14 The requirements according to this invention that the tube
15 sheets must be fabricated from a high-strength, solvent resistant
16 thermoplastic resin which is delivered to the hollow fiber membrane
17 fabric by extrusion at an elevated temperature to form a molten
18 band of potting material, yield tube sheets having performance
19 properties dramatically different than those produced by the
20 conventional technology. Among the performance advantages of the
21 tube sheets of the invention (and cartridges and modules containing
22 them) are the following: (1) the process of forming the tube sheets
23 can be automated - the fabric winding and tube sheet resin
24 deposition occur simultaneously and continuously; (2) the
25 automation ensures that the tube sheets will be highly uniform, and

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1 the resultant repeatability of the process makes possible its
2 quantitative optimization; (3) the potting resin is a thermoplastic
3 material chosen expressly for its optimum solvent resistance and
4 mechanical durability; (4) the need for the potting resin to have
5 a relatively low viscosity (as with the conventional gravity- and
6 centrifugal-potting methods) can be disregarded; (5) the wicking
7 problem is eliminated; (6) the limitations imposed by exothermic
8 potting resin curing reactions are eliminated, both because there
9 is no exotherm in the thermoplastic resin, and because the
10 progressive buildup of the tube sheets while the outer surface of
11 the nascent tube sheets rotates on the cartridge axis, promotes
12 heat dissipation; (7) the problems resulting from gaps and air
13 bubbles in the potting resin, potentially causing leaks in the
14 cartridge, are eliminated; (8) the tube sheets are neither rubbery
15 nor brittle, but plastic with high tensile- and flexural-modulus
16 and high strength (e.g., the tube sheet polymer has high elongation
17 at break), so the process of trimming the tube sheet ends to expose
18 the lumens is simple, reliable and does not itself damage the
19 hollow fibers; (9) module ports can be configured based on the
20 desired phase contact system design, disregarding the conventional
21 need for means for delivering potting resin to the bundle ends;
22 (10) since resin curing is immediately complete upon cooling as the
23 tube sheet is fabricated, there is no need to allow hours or even
24 days for the curing process, resulting in increased productivity;
25 and (11) according to preferred embodiments in which polyolefin
26 resins are used, these materials are virtually inert, resulting in

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1 substantial reductions in the handling dangers and ultimate
2 toxicity attending conventional resins such as polyepoxides and
3 polyurethanes. The elimination of the problems resulting from
4 gravity- or centrifugal- potting with exothermically-curing potting
5 resins yields a special advantage: according to the invention,
6 cartridges of any desired diameter can be uniformly potted in high
7 quality tube sheets. The size of the resulting cartridges is
8 limited only by the width of the hollow fiber membrane fabric and
9 the physical size of the cartridge-winding means. For example,
10 given a hollow fiber membrane fabric formed of 12 - foot long
11 hollow fibers, a module 12 feet long and 6 feet in diameter could
12 be made. Such a module would be large enough to handle industrial-
13 scale phase contact fluid processing needs.

14 We will now treat the various components of the cartridges and
15 modules in order, along with their means of assembly. This
16 discussion will first make reference to the conventional technology
17 for the materials, fabrication and operation of generally
18 conventional devices, and then return to the improvements according
19 to this invention. Although we assume the reader's understanding of
20 the conventional technology, further reference can be made to the
21 specific Examples and related Figures 1 - 6 below.

22 The hollow fibers suitable for use in the invention generally
23 include all such materials which can be formed into spiral-type
24 membrane-containing cartridges for separations and other phase

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1 contact applications. These hollow fibers may, for example, be
2 microporous, foraminous, or allow diffusion transfer. Hollow fibers
3 of relatively large diameter (sometimes referred to as "tubular
4 membranes") can also be used provided that they have sufficient
5 structural strength to maintain their shape in the bundle. Suitable
6 hollow fibers, described by dimensions and other structural
7 features, and including processes for such manufacture, are
8 disclosed, for example, in the following U.S. patents: Fujii U.S.
9 Patent No. 4,293,418; Kuzumoto U.S. Patent No. 4,430,219; Banner
10 U.S. Patent No. 4,758,341; Sekino U.S. Patent No. 4,781,834; Akasu
11 U.S. Patent No. 4,911,846; Caskey U.S. Patent No. 4,961,760; and
12 Bikson U.S. Patent No. 5,026,479. The hollow fibers can be
13 fabricated from any material demonstrating acceptable solvent
14 resistance and mechanical durability. Preferably, the hollow fibers
15 are made from a thermoplastic resin. More preferably, they are made
16 from the same thermoplastic resin as is selected as the solvent
17 resistant thermoplastic resin for potting the hollow fiber membrane
18 fabric. Most preferably, the hollow fibers are made from
19 polyolefins. The hollow fibers must be adequately capable of being
20 wet by contact with the chosen solvent resistant thermoplastic
21 potting resin. Polyolefin hollow fibers which are hydrophobic and
22 demonstrate desirable solvent resistance and mechanical durability,
23 and means for fabricating the same, are disclosed in Soehngen et al
24 U.S. Patent No. 4,290,987; Lowery et al U.S. Patent No. 4,405,688;
25 Lowery et al U.S. Patent No. 4,541,981; and Fisher et al U.S.

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1 Patent No. 5,013,439. It should be noted that the solvent
2 resistance of crystallizable polymers such as polyolefin materials
3 increases along with increasing crystallinity. Accordingly, steps
4 that can be conventionally undertaken to increase the crystallinity
5 of such hollow fibers (for example, annealing) will increase the
6 solvent resistance of the hollow fibers.

7
8 The selected hollow fibers are then fabricated into a fabric-
9 like array for assembly into the cartridge. Generally, the
10 principal benefit of incorporating the hollow fibers into a fabric-
11 like array rather than using loose fibers is that the fabric
12 structure holds adjacent hollow fibers in a spaced-apart, mutually
13 parallel relationship. This configuration promotes regularity of
14 the bundle and resultant uniformity in fluid flow dynamics. In
15 preferred embodiments, the hollow fibers constitute the weft of a
16 fabric, e.g., are placed transversely between warp filaments by the
17 guide elements of a loom. Given that the hollow fibers constituting
18 the fabric weft must be held in place by warp filaments, such warp
19 can take any form as taught in the art for fabric-like hollow fiber
20 arrays for spiral bundle production. For example, the warp
21 filaments can themselves be solid or also be hollow fibers, and the
22 fabric construction can be selected from the variety taught by the
23 art. The fabric can, alternatively, be prepared by substituting
24 warp for weft and weft for warp, so that the hollow fibers,
constituting the warp, are held by weft filaments. Hence, the terms

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1 "warp" and "weft" are used interchangeably hereinafter, and merely
2 designate two groups of filaments or fibers which are oriented
3 transversely to one another to yield a fabric-like web. The weft
4 fibers can be fabricated from any material demonstrating acceptable
5 solvent resistance and mechanical durability; preferably, they are
6 made from the same resin as is used to make the hollow fibers.
7 Suitable hollow fiber-containing fabric-like arrays, including
8 their construction, structure and performance, are taught, for
9 example, in the following U.S. patents: Kohl U.S. Patent No.
10 3,557,962; Barer U.S. Patent No. 4,460,641; Akasu U.S. Patent No.
11 4,911,846; and Baurmeister U.S. Patent No. 4,940,617; see also
12 European Patent Application No. 0,093,677, published November 9,
13 1983; and German Democratic Republic Patent Application No.
14 233,946, published March 19, 1986.

15
According to preferred embodiments, a rod-shaped core is
16 located at the longitudinal axis of the cartridge (if desired, this
17 core can be temporarily placed at the axis, and removed following
18 bundle fabrication). Although a solid rod can be used solely to
19 provide structural support for the cartridge, hollow core mandrels
20 are preferred. Core mandrels generally have a longitudinal axis and
21 a cylindrical exterior surface, an axial bore, and perforations
22 along the surface which communicate with the bore. Typical mandrels
23 have cylindrical interior and exterior surfaces; however it is
24 within the scope of the invention to employ mandrels having other

1 surfaces, for example, mandrels having multi-sided geometric cross-
2 sections (pentagonal, hexagonal, and the like), and mandrels whose
3 bores contain internal axial flow dividers or core plugs which are
4 installed or integrally formed in the mandrel. In this regard, the
5 term "cylindrical" as used herein refers to the general shape of a
6 hollow fiber membrane fabric after it has been spirally-wound onto
7 a cylindrical mandrel or core (or itself). Were, for example, a
8 mandrel of rectangular cross-section to be used (which use is
9 within the contemplation of the invention), then the resulting
10 spirally-wound bundle would tend initially to itself appear
11 rectangular with rounded corners, in cross-section (as the spiral
12 winding continues, such a bundle will gradually tend toward a
13 cylindrical cross-section). The purpose of the perforations along
14 the mandrel surface which communicate with the bore, is to
15 facilitate fluid flow between the bundle and the mandrel bore along
16 the mandrel's longitudinal axis. The mandrel perforations can take
17 various shapes, such as round holes and elongated slits. In cases
18 among the various embodiments of the invention in which it is
19 desirable to control flow volumes of fluid out of or into the
20 mandrel bore across its length, the mandrel perforations along the
21 length of the bore can be sized and shaped accordingly. The
22 perforations can also be confined to selected portions of the
23 mandrel length to control flow volumes and paths (e.g., co-current
24 or countercurrent). The overall length of the mandrel can also be
25 adjusted to suit particular needs. The mandrel should be fabricated
26 from a material demonstrating acceptable solvent resistance and

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1 mechanical durability. Preferably, the mandrel is made from a
2 thermoplastic resin. More preferably, the mandrel is made from the
3 same thermoplastic resin as is selected as the solvent resistant
4 thermoplastic resin for potting the hollow fiber membrane fabric.
5 Most preferably, the mandrel is made from a polyolefin resin.
6 Solvent resistant metals can also be used. Suitable mandrels are
7 disclosed in the following U.S. patents: Kuzumoto U.S. Patent
8 No. 4,430,219; and Caskey U.S. Patent No. 4,961,760.

9

10 The process steps discussed immediately below are carried out
11 conventionally, and as such will only be briefly mentioned. Further
12 information on them can be found, for example, in the following
13 U.S. patents: Caskey U.S. Patent No. 4,961,760; and Bikson U.S.
14 Patent No. 5,026,479.

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16 The fabric-like array is wound onto the mandrel surface (or
17 itself, if no mandrel is used) to form a spirally-wound,
18 cylindrically-shaped membrane bundle having two bundle ends
19 communicating with the mandrel bore. Assuming that the selected
20 fabric consists of hollow fiber weft held together by solid warp
21 filaments, then an end of the fabric is preferably aligned so that
22 the hollow fibers are substantially parallel to the mandrel axis,
23 the fabric end is attached to the mandrel (e.g. by clamping or
24 adhesive), and the assembly is wound up into a cylinder. If,

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1 alternatively, a fabric having both weft and warp hollow fibers is
2 used, then it may be desirable in certain applications to seal the
3 warp fibers into communication with the mandrel perforations, and
4 eliminate direct communication between the mandrel bore and the
5 shell-side region. It is well known in the art that hollow fiber-
6 containing fabric-like arrays can be wound helically onto a core
7 surface, so that the hollow fibers proceed along a helical path
8 with respect to the axis, with their two ends located at opposite
9 ends of the core. This invention can readily be practiced with such
10 arrays; it is also not strictly required (although preferred), that
11 the hollow fibers are mutually parallel.

12 Next, still referring to the conventional technology, the two
13 ends of the bundle are potted in resinous potting material serving
14 to seal each of the bundle ends into a monolithic tube sheet. A
15 variety of materials and several conventional methods for carrying
16 out potting to form tube sheets are well known in the art, as
17 shown, for example, in the Caskey U.S. Patent No. 4,961,760. When
18 the potting process is completed, a substantial portion of the
19 bundle (between the two tube sheets) will be free from resinous
20 potting material, and one or both of the potted ends of the bundle
21 are then trimmed so that the lumen ends of each hollow fiber at the
22 trimmed end(s) will be exposed.

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1 Finally, the potted bundle is fitted into a suitable housing
2 to constitute a module. Generally, the housing should have two open
3 ends and a cylindrical interior, and be suitably shaped to contain
4 the membrane bundle. After the bundle is installed in the housing,
5 the tube sheet(s) adjacent to the bundle end(s) with exposed lumens
6 is(are) sealed to the cylindrical interior of the housing, to
7 positively prevent fluid flow between the shell side and the lumen
8 side without passage through the membrane. At this point, the
9 cartridge has been divided into two regions mutually communicating
10 through the membrane including (1) a shell-side space which is
11 exterior to the portion of the bundle between the tube sheets and
12 is within the housing, and (2) a space including the hollow fiber
13 lumens and the exposed bundle end(s). Next, end cap means suitably
14 shaped to seal each of the two open housing ends are provided.
15 These end caps, together with the housing interior and the bundle
16 ends, serve to define two chambers, one or both of which
17 communicate with the membrane lumens. To facilitate fluid
18 introduction and recovery, suitable ports are provided for the
19 housing. In embodiments where no mandrel is present, the housing
20 must have at least one port communicating with the shell-side
21 space, arranged to permit fluid injection and withdrawal
22 therethrough. In embodiments including a mandrel, such ports are
23 optional. In all embodiments of the invention, the housing must
24 have at least one port communicating with the lumen side, arranged
25 to permit fluid injection and withdrawal therethrough. Multiple
26 ports can be provided, if desired. These considerations are further

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1 discussed in the prior art, including Caskey U.S. Patent No.
2 4,961,760.

3
4 According to the invention, the tube sheets must be fabricated
5 from a high-strength, solvent resistant thermoplastic resin, and
6 the resin must be extruded at an elevated temperature to form a
7 molten band of potting material that is directed onto the surface
8 of the hollow fiber membrane fabric to be potted. The thermoplastic
9 resin for use in accordance with the invention must exhibit the
10 following properties.

11 Melt Flow Index. This is the single most important factor in
12 choosing a thermoplastic resin for use. The thermoplastic must have
13 a melt flow index ("MI") which is high enough so that the resin
14 will flow during the potting process, and low enough so that it
15 will (1) remain where it is deposited (not "run") and (2) not
16 become brittle when it solidifies. The MI should broadly be between
17 about 0.01 to about 150 grams/10 minutes, preferably about 0.1 to
18 about 50 grams/10 minutes, more preferably about 1 to about 40
19 grams/10 minutes, and most preferably about 5 to about 20 grams/10
20 minutes (ASTM Method D1238-85; 2160 grams/10 minutes; all melt flow
21 index values in this application are tested and expressed using
22 this method and conditions; melt flow index should generally be
23 measured according to ASTM Method D1238-85, or if not specified
24 there, then at a temperature between about 50 to 70°C above the

1 sample's melting point). We note that resin viscosity is highly
2 relevant to conventional gravity- and centrifugal-potting methods,
3 because the ability of the resin to properly flow among the hollow
4 fibers is crucial. In practicing the methods of the invention,
5 however, melt flow index is the more appropriate measure of resin
6 flow properties, because of the high viscosity of the resins which
7 we employ. To illustrate the point, we consider polyethylene as an
8 example. For polyethylene, a melt flow index of 150 roughly
9 corresponds to a viscosity of 5,000,000 poise (at 190°C; 1 poise =
10 100 centipoise). A melt flow index of .01 for polyethylene, on the
11 other hand, theoretically corresponds to a viscosity of roughly
12 about 80,000,000,000 poise (at 190°C), and cannot be easily
13 measured - for that reason, such a viscosity is usually calculated
14 by converting a melt flow index measurement into viscosity. (A melt
15 flow index range of 5 - 20 for polyethylene corresponds to a
16 viscosity range of roughly about 200,000,000 poise to about
17 40,000,000 poise (at 190°C), again theoretically). The conversion
18 of viscosity data into corresponding melt flow index is carried out
19 by theoretical calculations as known by those skilled in the art.
20 The estimated viscosity values for polyethylene reported here were
21 calculated from measured melt flow index values according to
22 Equation 2.3-19 on page 46 of Transport Phenomena, R. Bird et al,
23 Wiley & Sons, New York; in combination with Figure 2 of ATSM Method
24 D1238-85, pp. 555 - 565. Similarly, elongation of the resin at
25 break (expressed as a percentage of the pre-stretched length) and
26 tensile- and flexural-modulus (normally expressed in megapascals,

1 or "MPa") both decrease with increasing melt flow index. Both high
2 elongation at break and modulus are desirable, and hence resins
3 having a relatively low melt flow index are preferred.

4 Melting Point. Thermoplastic polymers can be either
5 "crystalline" or amorphous. In general, no thermoplastic polymer is
6 completely "crystalline": there is always an amorphous component.
7 (The exception to this is single crystal polymers, which are
8 laboratory curiosities prepared on a minute scale at high expense).
9 On the other hand, an amorphous polymer can be completely
10 amorphous. Which designation (crystalline or amorphous) is given to
11 a particular polymer sample is simply a subjective judgement based
12 on the relative influence of crystalline and amorphous components
13 on the behavior of the sample. We explain this because it is the
14 crystalline portions of a thermoplastic resin, if any, that have a
15 true melting point temperature (T_m). The amorphous portions of
16 crystalline and amorphous materials will gradually soften rather
17 than melt. Hence, amorphous portions do not have a melting point.
18 In order to permit selection of thermoplastic resins suitable for
19 use in this invention, we need to establish objective tests. The
20 melting points of crystalline components can be measured
21 conventionally using a differential scanning calorimeter. One
22 common expression of the softening phenomenon in amorphous polymers
23 is the glass transition temperature (T_g), which is the temperature
24 at which the amorphous material changes between glassy and rubbery
25 states. The glass transition temperature can also be measured

1 conventionally using a differential scanning calorimeter. In the
2 case of a material having significant proportions of both
3 crystalline and amorphous components (i.e., a "crystalline"
4 polymer), both T_g and T_m can be measured. T_m will be higher than T_g
5 and will tend to govern the overall behavior of the polymer sample
6 in becoming sufficiently fluidized to enable its extrusion. In the
7 case of a truly amorphous polymer, there will be no T_m , and T_g will
8 govern the polymer's behavior. Another measure of both T_g and T_m is
9 the Vicat Softening Temperature (T_v), which is determined using ASTM
10 Designation: D 1525 - 91 "Standard Test Method for Vicat Softening
11 Temperature of Plastics". (See also, Whelan et al, The Dynisco
12 Extrusion Processors Handbook, page 34 (1988). In the case of a
13 crystalline polymer, T_v corresponds to T_m . For an amorphous polymer,
14 T_v corresponds to T_g . In accordance with the above, T_g , T_m and T_v of
15 a given polymer are measured as appropriate, and
16 determination is made as explained directly below, as to whether
17 the polymer can be used to practice the teachings of this
18 invention. (Where not explicitly designated, "melting point" means
19 T_m in the case of a "crystalline" polymer; and means T_g in the case
20 of a truly amorphous polymer; "Vicat Softening Temperature" will be
21 considered synonymous with T_m and T_g as explained above; it being
22 understood that these values are analogous measures of the
23 approximate point at which a resin at least begins to change from
24 a solid to liquid state). In general, a thermoplastic resin for use
25 according to the invention should melt at a temperature at least
26 about 10°C below the melting point of the chosen hollow fibers,

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1 more preferably at a temperature at least about 20°C below the
2 melting point of the chosen hollow fibers. Crystalline
3 polypropylene melts at about 160°C; hence, where crystalline
4 polypropylene hollow fibers are used, a polyethylene resin melting
5 at about 135°C or less is preferred for potting the tube sheets
6 (HDPE has a melting point of about 125°C to about 135°C; LLDPE has
7 a melting point of about 115°C to about 130°C; and LDPE has a
8 melting point of about 105°C to about 115°C).

9 Given the above requirements, any thermoplastic resin (1)
10 otherwise having appropriate solvent resistance for the solvent
11 environment in a particular desired end use application, and (2)
12 having adequate capability of wetting the surface of the chosen
13 hollow fibers (to result in a tube sheet without voids), can be
14 employed as the potting resin. As non-limiting examples, the
15 potting resin can be selected from homopolymers, copolymers,
16 mixtures and blends of the following: polyolefins, polycarbonates,
17 cellulosics, polysulfones, polyamides (including nylons),
18 polyesters, fluorine-plastics (including polytetrafluoroethylene),
19 polyacrylates and polystyrenes. (Blends are a special type of
20 mixture in which the components are mixed at a molecular level;
21 mixtures can be less homogeneous, and may have more than one
22 phase).

23 According to preferred embodiments, the thermoplastic potting
24 resin is a polyolefin homopolymer, copolymer, blend or mixture.

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1 For example, the resin can be polyethylene, polypropylene, poly-1-
2 butene, polypentene, polyhexene, polymethylhexene, polyheptene,
3 polymethylpentene, or crosslinkable polyethylene (in case of the
4 latter, the resin is applied at a suitable temperature to catalyze
5 the crosslinking reaction, resulting in enhanced solvent resistance
6 and mechanical properties). Other olefin polymers, e.g., block and
7 random copolymers of one or more olefins and non-olefins, as well
8 as blends and mixtures of these polymers can also be used. In
9 embodiments where such other olefin polymers are used, the
10 essential nature of the overall resin is preferably that of a
11 polyolefin - i.e., the polyolefin preferably constitutes at least
12 about 50%, more preferably at least about 60% of the overall
13 potting resin, and even more preferably, virtually 100% (by
14 weight). As we have previously noted 100% olefin polymers are most
15 preferred.

16 Crystallinity. Where a polyolefin potting resin is used, the
17 resin preferably exhibits a crystallinity of at least about 30%.
18 (Crystallinity is conventionally measured using differential
19 scanning calorimetry "DSC"). The solvent resistance of polyolefins
20 is directly proportional to their crystallinity. Accordingly,
21 polyolefin polymers with high crystallinity are most preferred.
22 Polyethylene by nature is crystalline, and the degree of
23 crystallinity can be controlled by copolymerization of ethylene
24 with higher ethylenically-unsaturated hydrocarbons. Depending on
25 the polymerization catalyst and process employed, polypropylene is

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1 either "crystalline" (i.e., about 60% crystalline and about 40%
2 amorphous by weight fraction) or amorphous (up to 100% amorphous,
3 by weight fraction). In the case of polypropylene, crystalline
4 polymer is normally acceptable; completely amorphous polypropylene
5 is less preferred. However, due to its nonpolar nature, even
6 completely amorphous polypropylene will demonstrate greater solvent
7 resistance than polyurethane or epoxy adhesives in particular polar
8 solvent environments. In the case of polyethylene, there are four
9 primary types of crystalline polymer to consider: high density
10 polyethylene ("HDPE", about 60% to about 80% crystalline); linear
11 low density polyethylene ("LLDPE", about 40% to about 60%
12 crystalline); low density polyethylene ("LDPE", about 30%
13 crystalline); and very low density polyethylene ("VLDPE", less than
14 about 30% to about 40% crystalline). All are acceptable, HDPE being
15 most preferred. Even VLDPE is advantageous where the potted
16 membranes will be exposed to polar solvents, because of its
17 nonpolar nature. Crystallinity of these polyethylene polymers is
18 proportional to the polymer density (degree of chain branching) in
19 grams/liter. For example, HDPE has a density of about 0.941 to
20 about 0.965g/ml; LLDPE has a density of about 0.916 to about
21 0.940g/ml; LDPE has a density of about 0.910 to about 0.925g/ml;
22 and VLDPE has a density of about .880 to about .910g/ml. Although
23 pure amorphous polymers are generally not preferred, they can be
24 used if blended or mixed with partially-crystalline polymers;
25 preferably the crystallinity (by weight fraction) of the overall
26 blend or mixture is at least about 30%. Other olefin polymers,

1 e.g., block and random copolymers of one or more olefins, can also
2 be used, the crystallinity again preferably being maintained at 30%
3 or higher.

4 Average Molecular Weight. Two commonly-accepted expressions of
5 the average molecular weight of a polymer are "weight average
6 molecular weight" and "number average molecular weight". We choose
7 to use the former. Weight average molecular weight (expressed in
8 grams/mole) is determined by calculating, for each molecular
9 component of the polymer sample, the molar weight of the component
10 in grams, and multiplying that molar weight by the mass of such
11 component in the sample; then taking the sum of such calculations
12 for each component; and finally, dividing the sum by the total mass
13 of the sample. Empirically, weight average molecular weight can be
14 determined by separating the components of the sample polymer from
15 each other, finding the mass of each, and performing the above
16 calculation. The separation can be done by (1) gel permeation
17 chromatography (which functions by size exclusion of the
18 components) or (2) dissolving the sample in a suitable solvent,
19 distilling the solution, and collecting the components separately.
20 The competing factors of (1) processability, which is optimized
21 with a low molecular weight polymer, and (2) mechanical properties
22 (including durability and resistance to cracking), which develop
23 with entanglement of polymer molecules, are optimized with a high
24 molecular weight polymer, should be balanced. Considering
25 thermoplastics generally, reliance on the above guidelines for melt

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1 flow index will be adequate to select appropriate polymers for use
2 as potting resins. According to preferred embodiments in which the
3 potting resin is a polyolefin, entanglement (using polyethylene as
4 an example) begins at a weight average molecular weight of about
5 1,250. More specifically, we have found that a weight average
6 molecular weight of at least about 10,000 (where polyethylene resin
7 is used) is preferred to ensure adequate mechanical properties.
8 Broadly, the polyolefin resin will preferably have a weight average
9 molecular weight between about 10,000 to about 500,000 grams/mole;
10 and more preferably, it has a weight average molecular weight
11 between about 20,000 to about 50,000 grams/mole. Ultra high
12 molecular weight polyethylene, which generally has a weight average
13 molecular weight of about 1,000,000 grams/mole or more (and is
14 about 70-80% crystalline) can be used, but its extrusion requires
15 very high pressure generally making its use less desirable.

16 For the remainder of this specification we will often refer
17 specifically to polyolefin resins as the preferred materials for
18 use as the potting resin. However, the invention is broadly
19 applicable to thermoplastic resins having the above-defined
20 required properties and optionally possessing the above-defined
21 preferred properties.

22 The solvent resistant polyolefin resins selected for use
23 according to preferred embodiments of the invention exhibit
24 viscosities above about 50,000 centipoise (corresponding to a melt

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1 flow index of about 150), and consequently cannot be effectively
2 used to pot the hollow fiber membrane fabric by gravity- or
3 centrifugal-potting techniques. Hence, according to the invention,
4 the preferred solvent resistant polyolefin resins are applied to
5 the surface of the hollow fiber membrane fabric simultaneously
6 while the hollow fiber membrane fabric is being wound to form a
7 spirally-wound, cylindrically-shaped membrane bundle. More
8 particularly, the fabric-like array is wound onto the mandrel
9 surface (or itself, if no mandrel is used) to form a spirally-
10 wound, cylindrically-shaped membrane bundle having two bundle ends
11 communicating with the mandrel bore. As the hollow fiber membrane
12 fabric is wound onto the mandrel surface, the fabric forms a nip
13 with the surface. The solvent resistant polyolefin resin is
14 extruded at an elevated temperature, yielding a molten band of
15 resin of suitable width and thickness to make the tube sheet; and
16 the molten band is continuously directed onto the surface of the
17 hollow fiber membrane fabric. By "extrusion" is meant a process of
18 forcibly driving the resin through a heated die, yielding a molten
19 continuous stream of resin shaped in accordance with the chosen
20 die. The temperature at which a given resin is extruded (i.e., as
21 it exits the extruder die) is preferably about 50 to 70°C above the
22 polymer's melting point. This will ensure that the resin is
23 sufficiently mobilized to flow, but not so fluidized that it will
24 "run" (not stay where it is deposited). However, the temperature of
25 the molten resin at the point of contact with the hollow fiber
26 membrane fabric must also be carefully chosen to be at least about

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1 10°C below the temperature at which the chosen hollow fibers begin
2 to melt or soften sufficiently to substantially deform or collapse
3 the lumens, more preferably at a temperature at least about 20°C
4 below such temperature for the chosen hollow fibers. The point of
5 contact temperature can be controlled by adjusting a variety of
6 parameters in a manner that those of ordinary skill in the
7 extrusion art will readily understand, including: the temperature
8 of the various heating zones of the extruder, especially at the die
9 orifice, the flow rate of the resin through the extruder, the take
10 up distance between the die orifice and the point of contact (which
11 allows the resin to cool), the speed of the advancing fabric,
12 thickness of the band of molten resin, and the temperature and
13 pressure applied by the compression roller (if employed). As the
14 fabric is wound up onto the core (or mandrel), the relative speeds
15 of travel of the core and extruder need to be adjusted: if the core
16 is driven at a constant speed (in revolutions/minute), its
17 circumference will steadily increase in speed. However, it is
18 preferable to adjust the extruder speed (upward) instead of
19 adjusting the core speed (downward), because (1) extruder speeds
20 can be easily adjusted, and (2) maintaining the speed of motion of
21 the molten resin in air constant (and high) will aid in maintaining
22 the resin point-of-contact temperature. The result of this process
23 is the application of solvent resistant resin lines at both bundle
24 ends beginning at the unwound edge of the fabric facing and
25 adjacent the nip with the axis, and proceeding along the fabric
26 edge, forming continuous tube sheets at both bundle ends extending

1 to the perimeter of the bundle. Preferably, the advancing molten
2 band makes contact with the fabric in the vicinity of the nip. In
3 one embodiment, the molten band makes contact with the side of the
4 fabric which faces away from the nip; optionally in conjunction
5 with this embodiment, a compressing roller meets with the molten
6 band in the vicinity of the nip to press the molten band into the
7 fabric. In another embodiment, the molten band makes contact with
8 the side of the fabric which faces toward the nip: in this case,
9 the nip itself presses the molten band into the fabric; optionally,
10 a compressing roller can be added to apply additional pressure.
11 This pressure should be regulated to ensure that the resin
12 adequately flows through the fabric to eliminate all gaps and
13 voids, but not so high that an inadequate amount of resin remains
14 among the fibers to seal them into a monolithic tube sheet. The
15 compressing rollers can be heated to a controlled temperature to
16 maintain fluidity of the solvent resistant resin as needed; or they
17 can be cooled to aid in heat dissipation and solidification of the
18 resin. The solvent resistant resin need not be directly employed to
19 fabricate a spirally-wound, cylindrically-shaped membrane bundle:
20 following extrusion, the molten band of resin can be allowed to
21 solidify, and subsequently can be re-heated by any suitable means
22 restoring it to a molten state while retaining its desired shape,
23 and then directed onto the fabric to produce a tube sheet.

24 In optional embodiments, the application of the molten band of
25 resin is discontinued after all of the desired hollow fiber

1 membrane fabric has been wound into the spirally-wound,
2 cylindrically-shaped membrane bundle but before the thickness of
3 the tube sheets (radius of the bundle measured from the
4 longitudinal axis of the mandrel) is sufficient for the tube sheets
5 to be sealed directly to the cylindrical housing interior. The tube
6 sheets are then extended by appropriate application of further
7 resin. For example, resin application is continued until the
8 desired tube sheet diameter is achieved. Alternatively, molds of
9 suitable size can be placed over the tube sheets of the potted
10 bundle after all of the hollow fiber membrane fabric has been
11 applied, and resin can be injected conventionally. If needed, the
12 tube sheets can be machined down to precise needed dimensions for
13 module installation. The tube sheets can then be sealed to the
14 cylindrical housing interior as needed, by simply applying an
15 appropriate amount of solvent resistant resin to the perimeters of
16 the tube sheets. Alternatively, ring-shaped fittings of appropriate
17 dimensions designed to tightly rest against the end of the
18 cylindrical housing interior can be fabricated (e.g., injection
19 molded), and adhesively attached to the perimeters of the tube
20 sheets.

21 **EXAMPLES**

22 Tube Sheet Preparation

23 Polypropylene hollow fiber membrane fabric samples were potted
24 according to the invention to form tube sheets, using each of the
25 four commercially-available polyethylene resins listed below in

1 Table 1. The apparatus is schematically illustrated in Figure 1.
2 Except in the cases of DOWLEX® 2035 and Dow 12350N polyethylene
3 resins, the polyolefin resin 10 was placed in a hopper 20 which fed
4 the resin 10 into a Hakke one-inch single-screw extruder 30 (25:1
5 length/diameter; 2:1 compression) fitted with a four-inch ribbon
6 die 40 (orifice thickness adjusted to 0.2 centimeters). In the
7 cases of DOWLEX® 2035 and Dow 12350N polyethylene resins, the same
8 procedure was followed except that the extruder was a Hakke one-
9 inch twin-screw extruder 30 (25:1 length/diameter; 2:1 compression)
10 fitted with a four-inch ribbon die 40 (orifice thickness adjusted
11 to 0.2 centimeters). The power supply for the extruder was a Hakke
12 Rheocord 90 development torque rheometer (not shown) which was
13 electrically wired to control the extruder screw speed and the
14 temperatures in zones 1 - 5 of the extruder barrel. The Rheometer
15 was set to control Zones 1 to 5 (the former being adjacent to the
16 hopper, and the latter being at the die orifice) successively
17 passed by the resin during extrusion, so that the desired resin
18 temperature was reached at the die orifice. The resin 10 exited the
19 extruder 30 through the ribbon die 40 having a rectangular orifice
20 (not shown) having a set width of 10 centimeters and thickness
21 adjusted to 0.2 centimeters, as a molten stream 50 of resin 10
22 moving in the direction of the arrow x. (In the Figure, three
23 molten streams 50 are depicted. In the actual trials, only one
24 ribbon die was used, and only one molten stream was produced, to
25 pot one end of the fabric bundle. However, the addition of a second
26 ribbon die to pot the other end of the bundle is shown for

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1 illustrative purposes. The third molten stream 50 between the other
 2 two, will be discussed later. (The ribbon die thickness was
 3 adjustable from .05 to .2 centimeters). The stream 50 of resin 10
 4 was stretched down by gravity to a width of about one inch over the
 5 take up distance and directed to make contact with the hollow fiber
 6 membrane fabric 60 fed from fabric feed roll 70 and advancing in
 7 the direction of the arrow y at a point 80 near the nip 90 formed
 8 between the mandrel 100 and the fabric 60, whereupon it continued
 9 to move in the direction indicated by the arrow z. An optional
 10 compressing roller 110 (which was used with (and only with) all
 11 trials on the Dow 12350N resin and on the Dow 17350N resin, and
 12 there unheated) forced the stream 50 of resin 10 into the fabric
 13 60. The mandrel 100 was advanced by a shaft driven by a variable-
 14 speed motor (not shown) to take up the advancing hollow fiber
 15 membrane fabric 60 potted with resin 10.

Table 1: Polyethylene Resins

<u>Name</u>	<u>Resin Type</u>	<u>Density¹</u>	<u>Melt Flow Index²</u>	<u>Melting Point¹</u>	<u>Elongation at Break¹</u>
DOWLEX® 2035	LLDPE	0.919	6.0	97°	650
HOSTALEN® GM 5010T2	HDPE	0.953	0.1	130	N.A. ⁴
HOSTALEN® GC 7260	HDPE	0.957	8.0	128	800+
Dow® 12350N	HDPE	0.950	12.0	123°	1,000
Dow 17350N	HDPE	0.950	17.0	123	900

¹ Grams per milliliter (g/ml).

² ASTM Method D1238-85; 190°C; 2160 grams/10 minutes.

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¹ Degrees Centigrade (°C.).

² Expressed as a percentage of the pre-stretched length.

³ DOWLEX® products are made by the Dow Chemical Company.

⁴ Vicat Softening Temperature in degrees Centigrade (°C.), this data point only; determined in accordance with ASTM - D-1525.

⁵ HOSTALEN is a registered trademark of Hoechst Aktiengesellschaft.

⁶ Data not available.

⁷ Available from the Dow Chemical Company.

1 The particular processing conditions which were employed with
2 each resin sample, and the qualitative results, are summarized in
3 Table 2. Additionally, in the Dow 12350N HDPE trial, the extruder
4 screws were turning at 33 rpm; Zones 1 - 5 of the extruder barrel
5 were set at 130°C, 155°C, 175°C, 175°C and 175°C, respectively; the
6 recorded polymer melt temperatures at Zones 3 and 5, respectively
7 were 185°C and 184°C; and the pressure in the barrel at Zones 3 and
8 5, respectively was 118 pounds per square inch (psi) and 173 psi.
9 In the Dow 2035 LLDPE trial, the extruder screws were turning at 44
10 rpm; Zones 1 - 5 of the extruder barrel were set at 325° Fahrenheit
11 (F), 425°F, 450°F, 460°F, and 460°F, respectively; the recorded
12 polymer melt temperatures at Zones 4 and 5, respectively were 444°F
13 and 525°F; and the pressure in the barrel at Zones 3 and 5,
14 respectively was 59 pounds per square inch (psi) and 70 psi.

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Table 2: Process and Results

<u>Name</u>	<u>Type</u>	<u>Extrusion Temperature¹</u>	<u>Take Up Distance²</u>	<u>Results</u>
DOWLEX® 2035	LLDPE	238	1.0	Good flow; sealed the fibers well.
HOSTALEN® GM 5010T2	HDPE	260	N.A. ³	Very poor flow; viscosity too high; unusable.
HOSTALEN® GC 7260	HDPE	190	0.5	Good flow; temperature too high; fibers damaged.
Dow 12350N	HDPE	175	0.5	Good flow; sealed the fibers well.
Dow 17350N	HDPE	160	0.5	Good flow; sealed the fibers well; the low extrusion temperature is an advantage.

¹ Die temperature (Zone 5) of extruder barrel in degrees Centigrade.

² Expressed in linear feet measured from the die orifice to the point of contact between the molten resin and the fabric.

³ Unmeasurable.

Discussion of Results

The DOWLEX® 2035 LLDPE having a MI of 6g/10 min flowed well and resulted in good sealing of the fabric. Although the extrusion temperature was very high, the take up distance was sufficient to cool the resin so that the hollow fibers were not damaged by the contact; and the resin's low melting point allowed it to remain molten despite the cooling.

The HOSTALEN® GM 5010T2 HDPE demonstrated very poor flow due to its extremely low melt flow index and consequent high melt viscosity. Adhesion of the resin to the hollow fibers was very poor and the potting was unsuccessful.

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1 The HOSTALEN® GC 7260 HDPE flowed well at an extrusion
2 temperature of 190°C. However, at this temperature and a take up
3 distance of 0.5 feet, the molten polyethylene started to melt the
4 hollow fibers on contact. Lowering the extrusion temperature or
5 extending the take up distance resulted in resin flow inadequate to
6 effectively pot the hollow fibers.

7 The Dow 12350N HDPE has a relatively high melt flow index
8 (12.0 g/10min.) compared with the other resins tested. This resin
9 flowed very well at a relatively low extrusion temperature (175°C).
10 The resin completely filled the spaces between the hollow fibers
11 and sealed all gaps. After complete curing, the tube sheet was cut
12 to yield cross-sectional samples of the potted hollow fibers.
13 Figures 2 and 3 respectively show optical microscope (magnification
14 factor of 20), and scanning electron microscope (magnification
15 factor of 250) cross-sectional views of hollow fibers in the tube
16 sheet. Both of these Figures confirm that there are no gaps around
17 the potted hollow fibers, and that the hollow fibers remain
18 cylindrical with unobstructed lumens.

19 Solvent Resistance Studies

20 We know from data available in the literature ("HOSTALEN® and
21 HOSTALEN PP®, Resistance to Chemicals and Other Media", Hoechst
22 Plastics, May 1987; and "Chemical Resistance of Plastic Molding
23 Materials", Dow Chemical Co., Plastics Dept., 1968) that the
24 solvent resistance of high density polyethylene is equivalent to or

1 better than that of polypropylene. As shown in Table 3 below, we
 2 would expect polyethylene to demonstrate equal performance (as
 3 compared with polypropylene) in methyl ethyl ketone, methyl
 4 isobutyl ketone and alcohol; better performance in amyl acetate,
 5 and slightly better performance in xylene.

Table 3: Solvent Resistance

<u>Name</u>	<u>Testing Temperature</u>	<u>MEK¹</u>	<u>MIBK²</u>	<u>AmAc³</u>	<u>Alcohol</u>	<u>Xylene</u>
PP ⁴	60°C	L ⁵	L	N ⁶	R ⁷	N
	20°C	R	R	L	R	H
HDPE	60°C	L	L	R	R	H
	20°C	R	R	R	R	L

¹ methyl ethyl ketone.

² methyl isobutyl ketone.

³ amyl acetate.

⁴ polypropylene.

⁵ resistant to a limited degree; swelling between 3 - 8 percent by volume.

⁶ not resistant; swelling in excess of 8 percent by volume.

⁷ resistant; swelling less than 3 percent by volume.

1 We carried out actual tests on the DOWLEX® 2035 LLDPE,
 2 HOSTALEN® GC 7260 HDPE, Dow 12350N HDPE and Dow 17350N HDPE with
 3 the same solvents to assess the solvent resistance of these resins.
 4 The tests were conducted by pouring resin pellets into aluminum
 5 weighing pans and heating the pellets in a convection oven for 30
 6 minutes at 180°C to produce disk-shaped resin samples. The disk-
 7 shaped samples were then immersed in the various solvents for the
 8 time periods indicated in Table 4, and swelling was monitored by
 9 measuring the weight increase of the samples. The results are

1 summarized in Table 4. The data show that the DOWLEX® 2035 LLDPE
 2 had poor solvent resistance, especially at 50°C. All three of the
 3 HDPE samples tested, HOSTALEN® GC 7260, Dow 12350N and Dow 17350N,
 4 demonstrated good solvent resistance overall, with limited
 5 resistance to xylene. Since HDPE yields much better results than
 6 LLDPE, these data confirm that high density (crystallinity) is
 7 important in providing good solvent resistance. Review of the melt
 8 flow indices of these resins shows that despite the lower melt flow
 9 index (higher molecular weight) of the DOWLEX® 2035 LLDPE, the
 10 three HDPE samples gave better results. This indicates that high
 11 density is more important than low melt flow index (high molecular
 12 weight) in determining resin solvent resistance.

Table 4: Solvent Resistance Tests

Name	Testing Temperature	Swelling ¹				
		MEK ²	MIBK ²	AmAc ³	ETOH ⁴	Xylene ⁵
DOWLEX® 2035	50°C	4.2	5.1	8.4	0.4	37
	R.T. ⁶	1.0	1.2	2.1	0.2	17
HOSTALEN® GC 7260	50°C	1.0	0.9	1.3	0	7.1
	R.T.	0.3	0.3	0.6	0	3.5
Dow 12350N	50°C	0.9	1.0	1.3	0.0	8.8
	R.T.	0.6	0.2	0.4	0.0	4.0
Dow 17350N	50°C	0.8	0.9	1.6	0.0	8.3
	R.T.	0.2	0.1	0.4	0.0	3.1

¹ methyl ethyl ketone.

² methyl isobutyl ketone.

³ amyl acetate.

⁴ expressed as a percentage of the pre-testing volume, by weight. Data were taken after fourteen days of continuous sample immersion in the solvent.

⁵ ETOH = 95% ethanol and 5% methanol (weight/weight).

⁶ Specifically, meta-xylene.

⁷ room temperature (about 25°C).

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1 In further optional embodiments, this invention can be
2 combined with the teachings of copending U.S. patent application
3 serial No.: 07/816,511 entitled, "Spiral-Wound Hollow Fiber
4 Membrane Fabric Cartridges and Modules Having Flow-Directing
5 Baffles", by simultaneously forming baffles in the bundle while
6 potting the bundle in tube sheets. Only the portions of those
7 teachings essential to an understanding of how to make such
8 combinations are set forth here. More particularly, that
9 application discloses the addition of at least one axially-
10 symmetrical baffle (hereinafter "sealing means") formed within the
11 shell-side region of the hollow fiber bundle in a shape which is
12 rotationally symmetrical about the axis. These sealing means create
13 radial cross-flow between the shell-side region and the hollow
14 fiber lumens; the benefits of such radial cross-flow include:
15 reduced channeling and development of boundary layers (tangential
16 flow of fluid past the hollow fibers without membrane surface
17 contact) and increased direct contact between fluids and membrane
18 surfaces (and hence, greater phase contact and more efficient
19 cartridge performance). The various process embodiments discussed
20 above concerning application of the molten resin to form the tube
21 sheets can also be applied to making the sealing means. As needs
22 dictate, the solvent resistant resins used to form the sealing
23 means and tube sheets can be the same or different; preferably, the
24 same resin is used.

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1 Referring to Figure 4, a schematic drawing of a module is
2 shown, in which hollow fiber fabric bundle (1) is contained in
3 housing (2), surrounding mandrel (12). A single radially-
4 symmetrical disc-shaped perimeter sealing means (3a, 3b) extends
5 from the perimeter (4a, 4b) of the bundle (1) to a distance (13a,
6 13b) from the mandrel (12), and a core plug (14) is provided in the
7 bore of the mandrel (12) at the point where the perimeter sealing
8 means (3a, 3b) approaches the surface of the mandrel (12). As shown
9 by the arrows (y, z), feed fluid enters the upstream mandrel port
10 (15), is forced radially outward by the core plug (14) into the
11 shell-side of the bundle (1), passes through the unobstructed axial
12 sub-portion (16a, 16b) of the bundle (1), and exits through the
13 downstream mandrel port (17). Since there is no blockage in the
14 bore of the mandrel (12) downstream of the single core plug (14),
15 the core plug (14) is preferably located near the downstream
16 mandrel port (17) to minimize stagnant areas in the shell-side
17 flow. Permeate is collected in the lumen-side and withdrawn at one
18 or both off-center lumen ports (18, 19) at the ends of the bundle
19 (1). Alternatively (not shown), feed can be introduced in the
20 lumen-side at one of the off-center lumen ports (18, 19) at the
21 ends of the bundle (1), and a sweep fluid can be introduced through
22 the upstream mandrel port (15) or downstream mandrel port (17) to
23 carry away permeate.

24 Shell-side fluid must be prevented from exterior channeling
25 whenever a bundle includes one or more perimeter sealing means -

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1 i.e., flow along the outside perimeter of the bundle. This is
2 accomplished by providing impermeable wrapping means covering the
3 exterior cylindrical surface of the bundle. This can be either a
4 coating or web-like impermeable layer or equivalent means affixed
5 to the exterior cylindrical surface of the bundle. When such a
6 wrapping means is present, perimeter sealing means are placed in
7 sealing engagement with the impermeable wrapping means. In
8 embodiments where no mandrel is present, an opening must be
9 provided in the impermeable wrapping means to allow at least one
10 port ("shell-side access means") communicating with the shell-side
11 space, to be placed on the side of the bundle. The edges of the
12 impermeable wrapping means surrounding the shell-side access means
13 should be sealed to the shell-side access means to prevent leakage
14 from the shell-side space.

15 In many cases it will be desirable to provide a hollow
16 mandrel, as discussed above, to serve as the core for the module.
17 In such cases, the feed fluid can be directed into the center of
18 the bundle through the mandrel, instead of being directed into a
19 side of the housing (the latter of which detracts from radial flow,
20 because the flow enters the bundle only on one side). In such
21 cases, it is necessary to supplement the radially-symmetrical
22 sealing means with one or more core plugs which may be installed or
23 integrally formed in the mandrel, to prevent the feed from simply
24 flowing straight through the mandrel bore without entering the
25 bundle. Core plugs in general are known in the art, as shown in the

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1 following U.S. patents:

2 Schell U.S. Patent No. 3,872,014; Foreman U.S.

3 Patent No. 4,033,878; Caskey U.S. Patent 4,961,760; Herczeg U.S.

4 Patent No. 4,997,564; and Reddy U.S. Patent No. 5,034,126.

5 Fabrication of the module schematically shown in Figure 4
6 proceeds as described above (the mandrel serving as the axis), the
7 tube sheets being formed simultaneously as the fabric is wound
8 until the fabric has been wound up to the predetermined distance
9 from its axis. As schematically shown in Figure 1 as the central
10 molten stream 50 of resin 10 (between the other two molten
11 streams), an additional molten band of solvent resistant resin
12 (which is preferably the same resin as is used to produce the tube
13 sheets, is then continuously applied along with the continuing
14 application of resin to form the tube sheets, beginning at the
15 unwound edge of the fabric facing and adjacent the nip with the
16 wound portion, and preferably at the midway point between the two
17 bundle ends, and proceeding in a line perpendicular to the axis
18 (x), forming a continuous seal extending to the perimeter of the
19 bundle. This seal has a planar disc-like monolithic shape.

20 Figure 5 schematically illustrates a module in which hollow
21 fiber fabric bundle (1) is contained in housing (2), surrounding
22 mandrel (12). A single radially-symmetrical disc-shaped axial
23 sealing means (20a, 20b) extends from the surface of the mandrel
24 (12) to a distance (11a, 11b) from the cylindrical housing interior

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1 (38), and a core plug (14) is provided in the bore of the mandrel
2 (12) at the point where the axial sealing means meets the surface
3 of the mandrel (12). As shown by the arrows (y, z), feed fluid
4 enters the upstream mandrel port (15), is forced radially outward
5 by the core plug (14) and axial sealing means (20a, 20b) into the
6 shell-side of the bundle (1), passes through the unobstructed
7 perimeter sub-portion (21a, 21b) of the bundle (1), and exits
8 through the downstream mandrel port (17). Again, since there is no
9 blockage in the bore of the mandrel (12) downstream of the single
10 core plug (14), the core plug (14) is preferably located near the
11 downstream mandrel port (17) to minimize stagnant areas in the
12 shell-side flow. Permeate is collected in the lumen-side and
13 withdrawn through the off-center lumen ports (18, 19) at one or
14 both ends of the bundle (1). Alternatively (not shown), feed can be
15 introduced in the lumen-side at one of the off-center lumen ports
16 (18, 19) at the ends of the bundle (1), and a sweep fluid can be
17 introduced through the upstream mandrel port (15) or downstream
18 mandrel port (17) to carry away permeate. As schematically shown in
19 Figure 1 as the central molten stream 50 of resin 10 (between the
20 other two molten streams), the axial sealing means (20a, 20b) is
21 constructed by continuously directing a molten band of solvent
22 resistant resin onto the hollow fiber membrane fabric
23 (simultaneously with the application of resin to form the tube
24 sheets), beginning at the module axis and proceeding in a direction
25 perpendicular to the axis outward along the unwound edge of the
26 fabric facing and adjacent the advancing nip with the wound

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1 portion, until the desired distance from the cylindrical housing
2 interior (38) is reached.

3 Figure 6 is a cross-sectional drawing of a module according to
4 Figure 5. This drawing shows a plurality of hollow fibers in the
5 bundle (1), drawn much larger than scale. The bundle (1) surrounds
6 a mandrel (12) centered on the axis (x), and is contained by a
7 housing (2). At the midpoint of the mandrel (12) is a core plug
8 (14), and adjacent thereto, an axial sealing means (20a, 20b). The
9 bundle (1) is potted at both ends in tube sheets (24, 25). End caps
10 (26, 27) are fitted over the tube sheets (24, 25) forming chambers
11 (28, 29). The housing (2) is fitted at both ends with o-rings (30,
12 31) in sealing engagement with the tube sheets (24, 25); and o-
13 rings (32, 33) in sealing engagement with the end caps (26, 27).
14 The mandrel (12) is fitted at both ends with tubes (34, 35) which
15 are each fitted with two o-rings (36, 37) in sealing engagement
16 with the bore of the mandrel (12) which respectively serve to guide
17 feed fluid from the upstream mandrel port (15) into the mandrel
18 (12), and from the mandrel (12) to the downstream mandrel port
19 (17). As shown by the arrows (y, z), feed fluid enters the mandrel
20 (12) through the upstream mandrel port (15), and is forced radially
21 through the shell-side of the bundle (1) by the core plug (14) and
22 axial sealing means (20a, 20b). The fluid flows through the
23 unobstructed perimeter sub-portion (21a, 21b) of the bundle (1),
24 and flows inwardly toward the mandrel (12) to exit as concentrate
25 through the downstream mandrel port (17). Permeate is collected at

1 the lumen-side port (18). A second lumen port (19) has been added
2 at the downstream end of the bundle (1). This modification makes it
3 possible to introduce a sweep fluid at one of the lumen ports (18)
4 and (19), and to withdraw it, together with feed fluid components
5 that have permeated from the shell-side space through the membrane,
6 at the other one of the lumen ports.

7 Attention should be paid to the width and thickness of the
8 molten bands of solvent resistant resin applied to produce the tube
9 sheets and sealing means, respectively. Concerning the tube sheets,
10 the width of the band as applied to the hollow fiber membrane
11 fabric is dictated by a balance of the competing goals to (1)
12 provide adequate adhesive force to prevent failure of the tube
13 sheets (the tube sheets must withstand the full operating pressure
14 of the cartridge), and (2) maximize the hollow fiber surface area
15 which is exposed to shell side fluid contact, and minimize the
16 distance between successive layers of hollow fiber membrane fabric
17 in the cartridge (thereby further maximizing the hollow fiber
18 surface area in the cartridge). Further, the thickness of the band
19 should be adjusted to both (1) provide enough volume of resin to
20 completely coat the portion of the hollow fibers to be potted,
21 while again (2) maximizing the hollow fiber surface area which is
22 exposed to shell side fluid contact. Preferably, an adjustable
23 ribbon die is used to extrude the resin. For example, a ribbon die
24 having an adjustable thickness of .05 - .2 centimeters and a width
25 of 4 inches can be used. The ribbon die dimensions and take up

1 distance are then empirically adjusted to result, after stretching
2 of the resin over the take up distance and according reduction in
3 its width and thickness, in a resin band of appropriate thickness
4 which will result in the formation of a tube sheet of desired
5 width. Typically, tube sheets having a width of about one to one-
6 and-one-half inches are preferred on bundles having a diameter up
7 to about 4 inches; bundles having larger diameters generally
8 require tube sheets of proportionately greater width.

9 Generally, the width of the axial- and perimeter-sealing means
10 can be more narrow than that of the tube sheets, because (1) it is
11 desirable to minimize the shell-side space consumed by the sealing
12 means and attendant reduction in the module's mass transfer
13 efficiency, and (2) the sealing means need not withstand the full
14 operating pressure. In additional embodiments, one or more of each
15 of the above two types of sealing means are employed together.
16 Although the discussion above has been directed to sealing means in
17 planar disc form oriented perpendicular to the module axis, sealing
18 means having other shapes which are axially-symmetrical and
19 rotationally symmetrical about the axis may be provided where
20 desired.

21 The extrusion dies to be employed can be chosen on a case by
22 case basis, as dictated by the needed shape, size and number of
23 molten resin bands. Where a cartridge having tube sheets at both
24 ends is to be made, a die having two orifices appropriately spaced

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1 and positioned is preferably used. If one or more sealing means are
2 to be fabricated in the bundle, appropriate further die orifices
3 can be added, together with means to open and close the orifices as
4 needed to make the sealing means. Such opening and closing means
5 can be automatically controlled. In preferred embodiments, dies
6 that will produce ribbon-shaped bands of molten resin (ribbon dies)
7 are employed: whereas the width of the bands must be sufficient to
8 withstand operating pressures, the relative thickness of the
9 deposited resin should be consistent with the thickness of the
10 fabric.

11 In a particularly preferred embodiment of the invention, the
12 components of the cartridge (hollow fiber membrane fabric and
13 solvent resistant resin) are all polyolefin materials. In this
14 manner, the materials constituting the hollow fiber membrane fabric
15 and solvent resistant resin can be matched in terms of solvent
16 resistance to specific classes of solvents. Hence, the overall
17 nonpolarity of the cartridge, its resistance to polar solvents, and
18 predictability of the cartridge's performance in particular
19 application environments can be simultaneously maximized.

20 Whereas the cartridge components are fabricated from polymeric
21 materials in part due to processability requirements, the other
22 components making up a module can be chosen from a wide range of
23 materials which have even greater solvent resistance and mechanical
24 durability. However, in particular applications, fabrication of

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1 some or all module components from polyolefin materials may also be
2 desirable.

3 The spiral-type hollow fiber membrane fabric-containing
4 cartridges and modules of the invention are generally operated in
5 a manner similar to conventional cartridges and modules.
6 Accordingly, suitable operating procedures are disclosed in the
7 following U.S. patents:

8 Banner U.S. Patent No. 4,758,341; Holland U.S.
9 Patent No. 4,855,058; and Caskey U.S. Patent No. 4,961,760. More
10 particularly, a fluid can be introduced into the bundle lumens at
11 either or both potted ends, and allowed to diffuse out of the
12 fibers into the shell-side region. The permeated fluid can then be
13 collected at either the mandrel (through the perforations) or at
14 the cartridge perimeter, or both. Alternatively, a fluid can be
15 introduced at one or both ends of the mandrel through the bore and
16 allowed to diffuse through the mandrel perforations into the shell-
17 side region. Fluid which permeates through the fibers into their
18 lumens can then be collected at one or both of the potted bundle
19 ends; and concentrate remaining in the shell-side region can be
20 collected at the cartridge perimeter. Ports to facilitate these
21 permutations can be built into the module housing at the bundle
22 ends and on the cylindrical exterior of the housing as needed.

23 End use applications for the spiral-type hollow fiber membrane
24 fabric-containing cartridges and modules of the invention include

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1 the end uses for conventional cartridges and modules as disclosed
2 in the art. For example, the end uses disclosed in the following
3 U.S. patents are contemplated: Holland U.S. Patent No. 4,855,058;
4 Baurmeister U.S. Patent No. 4,940,617; and Caskey U.S. Patent No.
5 4,961,760. In general, gaseous fluids will flow more evenly and
6 freely through the bundle than liquids, whose resistance to free
7 flow increases with viscosity.

8
9 While several embodiments of the invention have been
10 illustrated and described above, it is not intended to be limited
11 to the details shown, since various modifications and structural
12 changes may be made without departing from the spirit of the
present invention, which is defined by the claims below.

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1 WE CLAIM:

2 1. A method of fabricating a spiral-type hollow fiber membrane
3 fabric-containing cartridge including tube sheets having improved
4 solvent resistance and mechanical durability, comprising the
5 following steps:

6 a. forming a plurality of hollow fiber membranes each having
7 a lumen, into a fabric-like array having a warp and a
8 weft, in which the hollow fibers substantially are
9 mutually-parallel and constitute the fabric weft, and are
10 held in spaced-apart relationship by filaments
11 constituting the fabric warp; then

12 b. winding the array upon an axis which is substantially
13 parallel to the hollow fibers into a spirally-wound
14 membrane bundle having two bundle ends and a cylindrical
15 exterior surface; and

16 c. simultaneously with step (b.), extruding in molten form
17 a high-strength, solvent resistant thermoplastic resin
18 having a melting point at least about 10° Centigrade
19 below the melting point of the hollow fibers, and having
20 a melt flow index between about 0.01 to about 150
21 grams/10 minutes; and directing said resin onto each of
22 the two bundle ends to thereby pot each of the two bundle
23 ends in said resin, serving to seal the bundle end into
24 an adjacent monolithic tube sheet, a portion of the
25 bundle between the two tube sheets being free from resin

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1 to form a shell-side region; and then
2 d. exposing the lumen ends of the hollow fibers constituting
3 at least a first one of the bundle ends to communicate
4 with the exterior of the bundle.

5 2. The method of claim 1, in which the high-strength, solvent
6 resistant thermoplastic resin has a melting point at least about
7 20° Centigrade below the melting point of the hollow fibers.

8 3. The method of claim 1, in which the high-strength, solvent
9 resistant thermoplastic resin has a melt flow index between about
10 0.1 to about 50 grams/10 minutes.

11 4. The method of claim 1, in which the high-strength, solvent
12 resistant thermoplastic resin has a melt flow index between about
13 1 to about 40 grams/10 minutes.

14 5. The method of claim 1, in which the high-strength, solvent
15 resistant thermoplastic resin has a melt flow index between about
16 5 to about 20 grams/10 minutes.

17 6. The method of claim 1, in which the axis is constituted by a
18 hollow mandrel having a longitudinal axis and a cylindrical
19 exterior surface, an axial bore, and perforations along the surface
20 which communicate with the bore.

1 7. The method of claim 1, in which the lumen ends of the hollow
2 fibers constituting both of the bundle ends are exposed to
3 communicate with the exterior of the bundle.

4 8. The method of claim 1, comprising further steps as follows:

5 e. subsequent to step (b), covering the cylindrical exterior
6 surface of the bundle with an impermeable wrapping means;
7 and

8 f. simultaneously with step (b), forming at least one
9 axially-symmetrical sealing means from high-strength,
10 solvent resistant thermoplastic resin within the shell-
11 side region in a shape which is rotationally symmetrical
12 about the axis, said sealing means being in sealing
13 engagement with the impermeable wrapping means and
14 extending to a distance away from the axis, forming an
15 axial sub-portion of the shell-side region which is
16 unobstructed to fluid flow, said sealing means dividing
17 the shell-side region into two shell-side portions in
18 mutual fluid communication through the sub-portion.

19 9. The method of claim 1, comprising further steps as follows:

20 e. simultaneously with step (b), forming at least one
21 axially-symmetrical sealing means from high-strength,
22 solvent resistant thermoplastic resin within the shell-
23 side region in a shape which is rotationally symmetrical
24 about the axis, said sealing means intersecting the axis

1 and extending to a perimeter which is located at a
2 distance away from the cylindrical housing interior,
3 forming a sub-portion of the shell-side region between
4 the cylindrical interior of the housing and the perimeter
5 of the sealing means which is unobstructed to fluid flow,
6 said sealing means dividing the shell-side region into
7 two shell-side portions in mutual fluid communication
8 through the sub-portion.

9 10. The method of claim 1, in which the high-strength, solvent
10 resistant thermoplastic resin is a polyolefin homopolymer,
11 copolymer, blend or mixture comprising one or more members of the
12 group consisting of polyethylene, polypropylene, poly-1-butene,
13 polypentene, polyhexene, polymethylhexene, polyheptene and
14 polymethylpentene having: a crystallinity of at least about 30%;
15 and a weight average molecular weight between about 10,000 and
16 about 500,000 grams per mole.

17 11. The method of claim 10 in which the high-strength, solvent
18 resistant thermoplastic resin is a high density polyethylene
19 homopolymer having a crystallinity of about 60% to about 80%.

20 12. The method of claim 10 in which the high-strength, solvent
21 resistant thermoplastic resin has a weight average molecular weight
22 between about 20,000 to about 50,000 grams/mole.

1 13. The method of claim 1, in which the hollow fibers are made
2 from a high-strength, solvent resistant thermoplastic resin which
3 is a polyolefin homopolymer, copolymer, blend or mixture comprising
4 one or more members of the group consisting of polyethylene,
5 polypropylene, poly-1-butene, polypentene, polyhexene,
6 polymethylhexene, polyheptene and polymethylpentene.

7 14. The method of claim 13, in which the hollow fibers are made
8 from a polypropylene homopolymer having a melting point of about
9 160° Centigrade, and the high-strength, solvent resistant
10 thermoplastic resin is a polyethylene homopolymer having a melting
11 point of about 135° Centigrade or less.

12 15. A spiral-type hollow fiber membrane fabric-containing
13 cartridge including tube sheets having improved solvent resistance
14 and mechanical durability, fabricated by the method of claim 1, 6,
15 7, 8, 9, 10, 11, 13 or 14.

16 16. A method of fabricating a spiral-type hollow fiber membrane
17 fabric-containing module including tube sheets having improved
18 solvent resistance and mechanical durability, comprising the
19 following steps:

- 20 a. forming a plurality of hollow fiber membranes each having
21 a lumen, into a fabric-like array having a warp and a
22 weft, in which the hollow fibers substantially are
23 mutually-parallel and constitute the fabric weft, and are

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- 1 held in spaced-apart relationship by filaments
2 constituting the fabric warp; then
- 3 b. winding the array upon an axis which is substantially
4 parallel to the hollow fibers into a spirally-wound
5 membrane bundle having two bundle ends and a cylindrical
6 exterior surface; and
- 7 c. simultaneously with step (b.), extruding in molten form
8 a high-strength, solvent resistant thermoplastic resin
9 having a melting point at least about 10° Centigrade
10 below the melting point of the hollow fibers, and having
11 a melt flow index between about 0.01 to about 150
12 grams/10 minutes; and directing said resin onto each of
13 the two bundle ends to thereby pot each of the two bundle
14 ends in said resin, serving to seal the bundle end into
15 an adjacent monolithic tube sheet, a portion of the
16 bundle between the two tube sheets being free from resin
17 to form a shell-side region; then
- 18 d. exposing the lumen ends of the hollow fibers constituting
19 at least a first one of the bundle ends to communicate
20 with the exterior of the bundle; then
- 21 e. inserting the bundle into a housing for the bundle having
22 first and second housing ends and a cylindrical housing
23 interior and being suitably shaped to contain the
24 membrane bundle, having means adjacent the first housing
25 end sealing the tube sheet adjacent the first bundle end
26 to the cylindrical housing interior, said housing which

1 contains the bundle defining two regions mutually
2 communicating through the membrane including (1) a shell-
3 side space exterior to the portion of the bundle between
4 the tube sheets and within the housing, and (2) a space
5 including the hollow fiber lumens and the first bundle
6 end; then

7 f. applying first end cap means adjacent the first housing
8 end and suitably shaped, together with the cylindrical
9 housing interior and the first bundle end, to seal the
10 first housing end and define a first chamber
11 communicating with the membrane lumens; and

12 g. applying second end cap means adjacent the second housing
13 end and suitably shaped, together with the cylindrical
14 housing interior and the second bundle end, to seal the
15 second housing end and define a second chamber; and

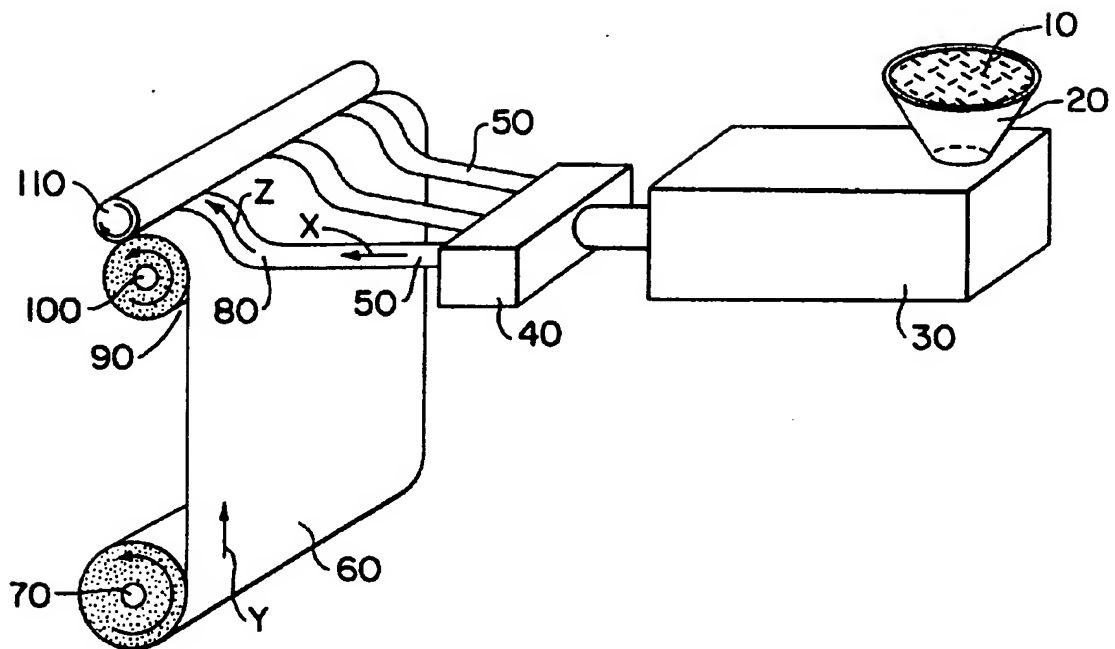
16 h. providing shell-side access means in the housing,
17 including at least one port communicating with the shell-
18 side space, arranged to permit fluid injection and
19 withdrawal therethrough; and

20 i. providing at least one port communicating with the first
21 chamber in the housing, arranged to permit fluid
22 injection and withdrawal therethrough.

23 17. A spiral-type hollow fiber membrane fabric-containing module
24 including tube sheets having improved solvent resistance and
25 mechanical durability, fabricated by the method of claim 16.

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FIG. 1



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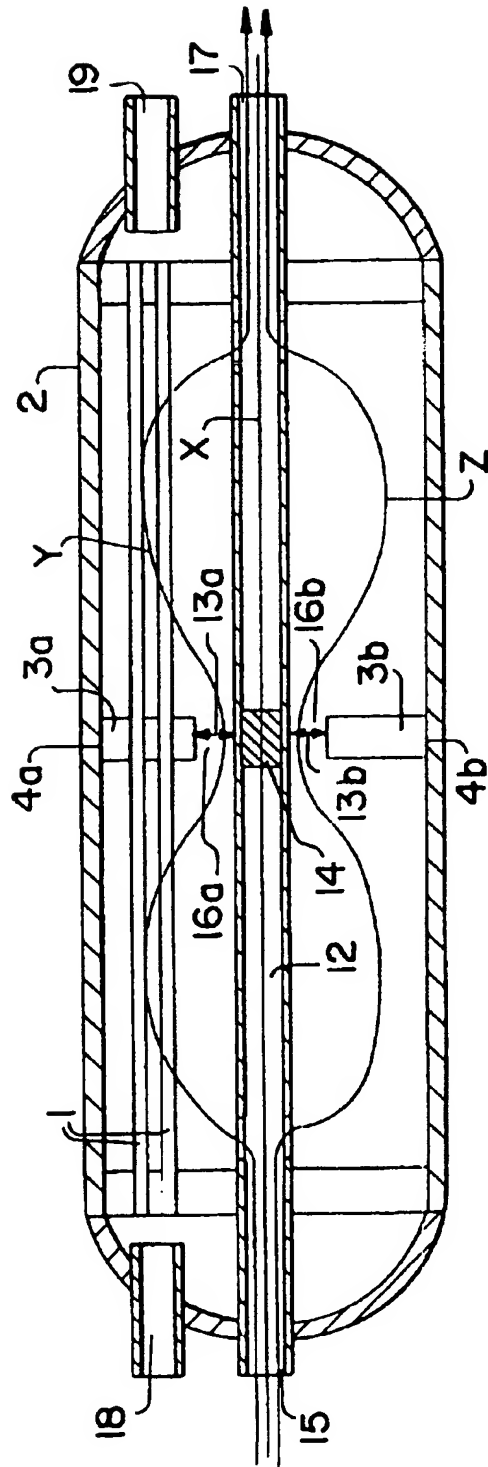


FIG. 4

Patented May 19, 1941
Smart & Biggar

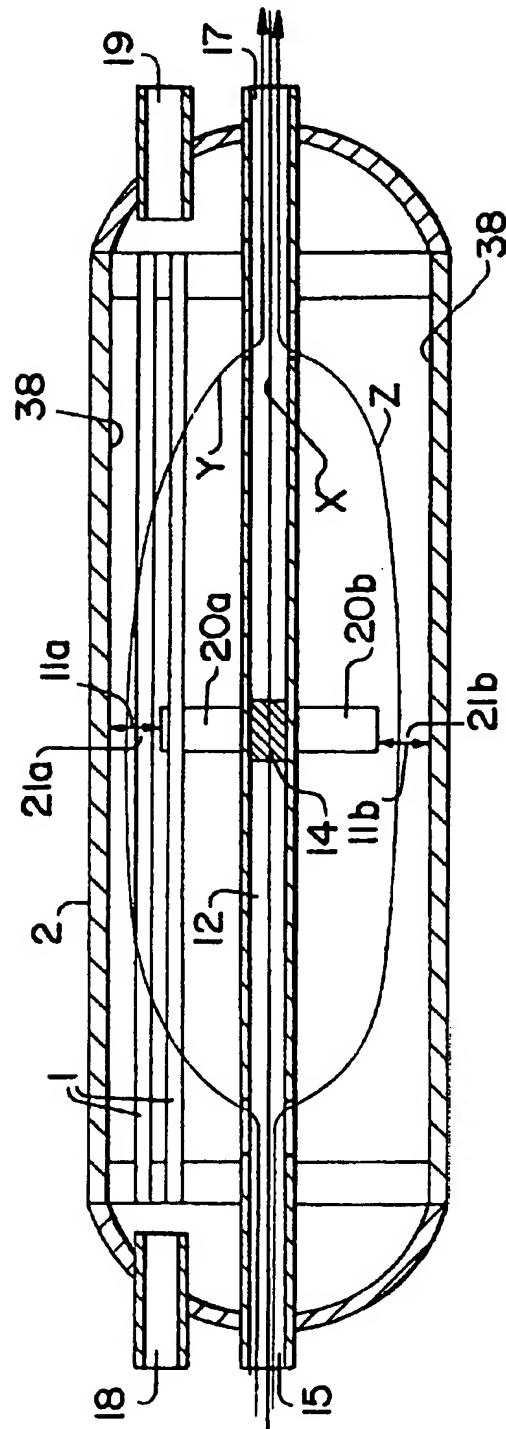


FIG. 5

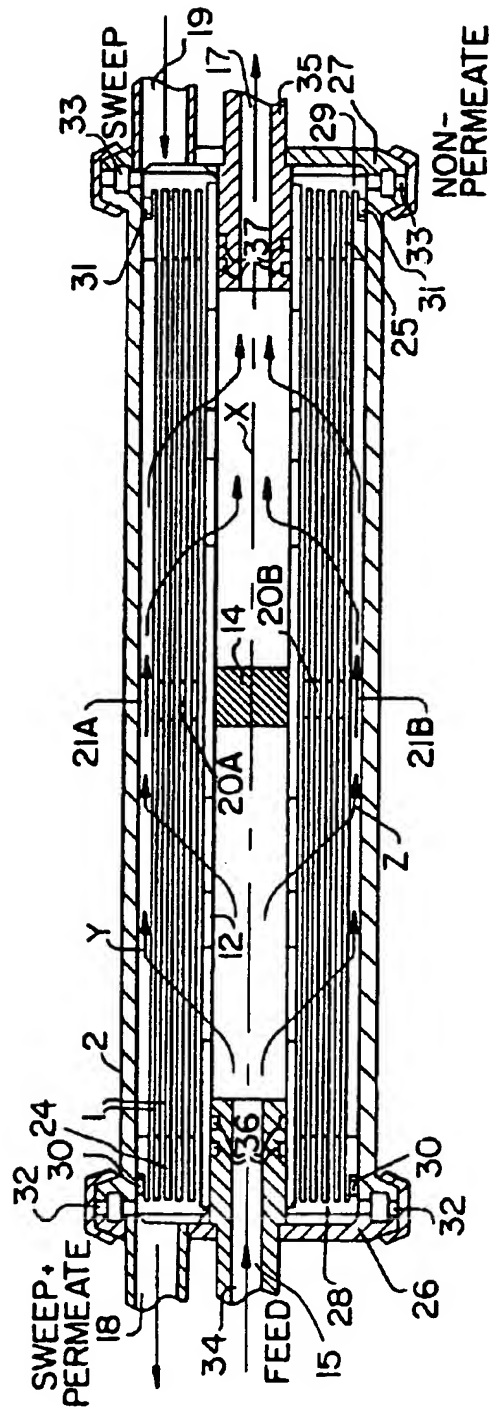


FIG. 6

UNSCANNABLE ITEM

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(ITEM ON THE 10TH FLOOR ZONE 5 IN THE FILE PREPARATION SECTION)

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NE POUVANT ÊTRE BALAYÉ

(DOCUMENT AU 10 IÈME ÉTAGE AIRE 5 DANS LA SECTION DE LA
PRÉPARATION DES DOSSIERS)

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